Conference Paper

Problems of Operation of Elastomer Materials in The Arctic Region

N.N. Petrova, V.V. Portnyagina, V.V. Mukhin, and E.S. Kyzmina

North-Eastern Federal University, Institute of Natural Sciences, 677000 Yakutsk, Russia

Abstract

The operability of frost-resistant industrial sealing rubbers on the basis of full-scale exposure of rubber samples in the environment of oil in cold climate has been investigated. It is found that interaction of rubbers with oil media (fuel, lubricants) causes diffusion of a plasticizer from the elastomer material into the contacting medium and decrease of frost resistance coefficient. Choosing the material for production of different seals for the conditions of the North one must use rubbers with significant temperature range of operation, for example propylen-oxide elastomer, which is highly frost resistant and has a stable set of operational properties.

Keywords: rubber, frost resistant, oil resistant, climatic stability, Arctic region

Corresponding Author: N.N. Petrova; email: pnn2002@mail.ru

Received: 9 September 2016
Accepted: 19 September 2016
Published: 12 October 2016

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the ASRTU Conference Committee.

1. Introduction

Over the last decade, Arctic has become a region interesting for the global community. It is noteworthy that the Arctic today is not only in the sphere of geopolitical interests of circumpolar nations (Russia, USA, Canada, Denmark, and Norway), but for other countries located far from the region (China, Japan, South Korea). So, the Kiruna Declaration of 15.05.2013 provided observer status to China, South Korea, Italy, India, Japan, and the European Union. The Arctic is the last unspoiled natural pantry, a huge reserve of minerals. Development of the Arctic region only can be performed due to the huge infrastructure cost, required reliable equipment, and new polymer materials.

Let us consider the problem of climatic stability of polymer materials and products on the example of exploitation of rubber in cold climate. General body of sealing details for modern technique is produced of different kinds of rubbers. The number of rubber parts in a modern vehicle or device can reach thousands of items. High elasticity, ability to undergo long-term multiple deformations, tolerance to influence of diverse aggressive media, and manufacturability make rubber an irreplaceable material for producing different sealing devices.

The Republic of Sakha (Yakutia) is the largest northern region of Russia. Sakha is rich in raw materials (oil, gas, coal, and diamonds). Yakutia is also known for its cold climate. Such peculiarities of Yakutia climate as extremely low temperatures in winter, sharp oscillations of temperature in spring and autumn with passing zero twice a day, high intensity of solar radiation seriously affects the properties of materials, especially polymer materials. Ageing of polymers in these conditions is faster, negative impact is higher. Under these conditions, the ambient temperature range in which the technical properties of materials, structures, and assemblies must provide the required reliability and durability, is usually taken from -60 to + 60°C. Different investigations have shown that only a limited amount of rubbers can be used reliably in extremely harsh conditions, which holds back the development of the Northern Territories. For example, more than 30% of all cases of working capacity loss of machines and mechanisms in Yakutia are associated with insufficient frost resistance of various rubber parts; downtime for this reason is up to 40% [1, 2].

While studying the possibility of exploitation of rubber in certain conditions, it is vitally important from a practical point of view to determine climatic stability of elastomer materials, which are usually assessed by changing the performance properties of the materials. For this purpose, environmental chambers simulating cyclic change in temperature or accelerated testing at elevated temperature are applied. Typically, in laboratory conditions it is not possible to simulate the behavior of elastomer materials under the combined effect of different climatic and operational factors, so for a reliable assessment of their performance full-scale testing in natural conditions is required. We have performed investigations devoted to rubber behavior in Talakan oil under the conditions of in-cite exposition after relatively long periods of time (2 years). We chose this oil as the medium for simulating impact on rubber of lubricating oils, fuels, which are used in technique and are hydrocarbon nature. We have discussed main test results and suggested the new ways of creating frost resistant elastomer materials.

2. Methods

We studied different grades of industrial rubbers based on butadiene-nitrile rubber (NBR), which are characterized relatively high frost resistance (Tg= -50°C) and oil-resistant: B-14 и 7B-14-1, 7130, 7455, 7257-6, 7-129-K. These rubbers use as frost resistant sealing materials for production of cuffs, gaskets, and seals. We have also produced and investigated rubber based on new propylene-oxide rubber (SKPO), which is copolymer of propylene-oxide and allyl glycidyl ether, and epichlorohydrin rubbers, which is terpolymer of propylene oxide, epichlorohydrin, and allyl glycidyl ether. The distinctive properties of SKPO are unique frost resistance (T_g = -74°C), ozone and heat resistance [3]. Epichlorohydrin rubber has less frost resistance (T_g=-60°C), than propylene-oxide rubber, but its resistance to oils higher than SKPO. The rubbers were made in «BRABENDER PL-2200-3» plasticorder. Rubber blends contained all ingredients for rubber preparation like: dispersant, sulfur, vulcanization accelerators, and activators, filler, antiaging agent, plasticizer.

To determine the influence of climatic factors, the rubber samples (plates and stubs) were placed into oil from Talakan deposit for long-term exposition (not less than two years) in the cold depot under the climatic conditions of Yakutsk. The oil is characterized by relatively low contents of sulfur (0.59 %), is gummy, paraffin and contains fractions steaming away at 350°C to 49.1 %. Once in two months the samples were taken out of oil and tested according to standard methods: their physical and mechanical

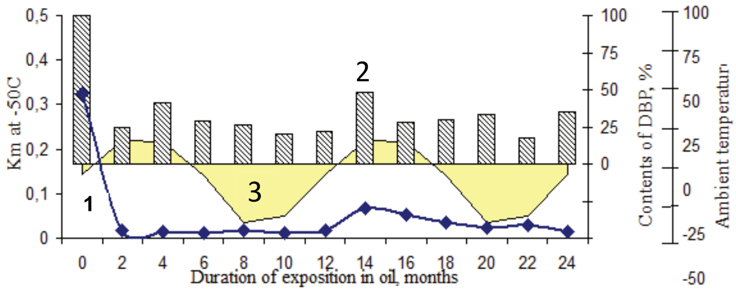

Figure 1: Dependence of frost resistance coefficient at -50°C (1), plasticizer contents (2) in B-14 rubber and ambient temperature (3) on duration of detention in oil under the conditions of in-cite exposition.

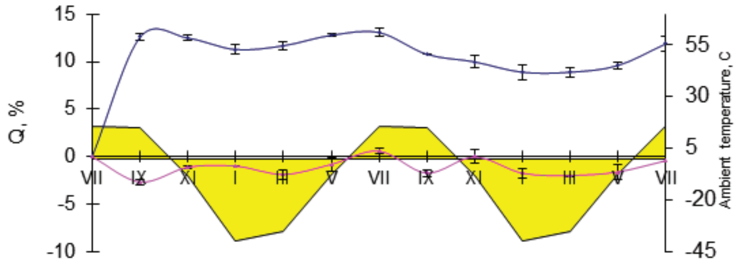

Figure 2: Dependence of the rubber swelling degree on time of exposition in oil under natural conditions: 1 – SKPO; 2 – 7130; 3 – ambient temperature.

indices were determined (σp - conventional strength with elongation, ε_p- elongation at break, GOST 270-84) [4]; frost resistance coefficient from elastic recovery after compression (Km, GOST 13808-79) [5]; swelling degree in the hydrocarbon medium (Q, GOST 9.030-74) [6]; residual deformation with compression (C, GOST 9.029-74) [7]. Contents of the plasticizer in the rubber were determined using IR-spectroscopy.

3. Results

Variations of the listed rubber parameters (σp, Km, Q, C,) as they were exposed in oil at ambient temperatures significantly depend on physical, mechanical, and low-temperature properties of the polymer base, depth of thoroughgoing ageing processes, intensity of climatic factors, and for elastomer materials based on butadiene-nitrile rubber they are of general character. After some variation in the initial period of exposition strength properties of the most rubbers are generally permanent, i.e. we did not observe intense destruction of the polymer chains after two-year exposition in oil. The same was observed in case of residual deformation of compression, which characterizes the material's ability to elastic recovery after unloading and relative elongation with rupture. Their strongest influence was observed on the rubber swelling and frost resistance coefficient (Figs. 1-3).

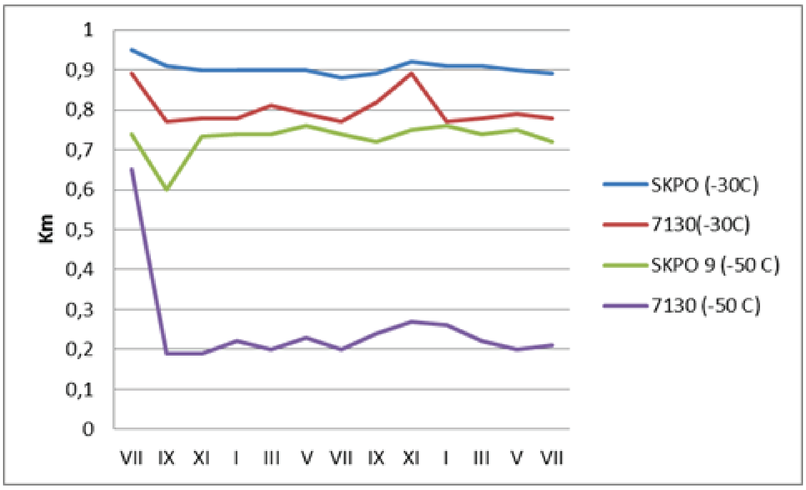

Figure 3: Dependence of frost resistance coefficient (Km) determined from elastic recovery after compression on time of exposition in oil under natural conditions: 1 – SKPO (-30∘C); 2 – SKPO (-50∘C); 3 – 7130 (-30∘C); 4 – 7130 (-50∘C).

After interaction of rubbers with hydrocarbon media one can observe, on the one hand, swelling of the material resulting in weakening of intermolecular interaction and degradation of strength. On the other hand, some ingredients, which are soluble in the medium, wash out from the rubber mixtures. Usually, they are plasticizers aiming at increasing rubber frost resistance. Content of the plasticizers in rubber mixers is very high from 20 to 40 %. Injection of plasticizers raises kinetic flexibility of rubber chains and decreases glass-transition temperature of the system.

Swelling degree of rubber characterizes the summary influence of all diffusion processes including both hydrocarbons penetration and plasticizers washing out. For all studied butadiene-nitrile rubbers swelling degree was within the area of negative values, for rubber based on SKPO it was close to that of the typical curve of restricted polymer swelling in hydrocarbon media (Fig. 2). The results of IR-spectroscopy showed that washing out of the plasticizer occurred intensely as well (Figs. 4, 1). As was shown after first two-month exposition in Talakan oil (from April to June) frost resistance coefficient of rubber BNR B-14 decreased by 80-94% due to washing out of plasticizers (Fig. 1). As is well known [3], to provide safe operation of immovable sealing details in the regions with cold climate, allowable threshold of values of the coefficient of frost resistance at -50°C should be set to 0.2, i.e. studied rubbers after short-term exposition in hydrocarbon medium become unserviceable for extreme climatic conditions.

Unlike BNR, new polypropylene-oxide rubber performs stable high values of frost resistance coefficient due to chemical nature of the polymer base (Fig. 3). All temperature tests showed that propylene-oxide rubber lain within the area of developed highly elastic state and made the basic contribution into the general value of frost resistance coefficient, washing out of plasticizers does not affect Km of rubber (Figs. 3,4). Environmental testing of rubbers based on epichlorohydrin rubber is not finished yet, but the first results confirm the main trends obtained for rubbers based on SKPO elastomer.

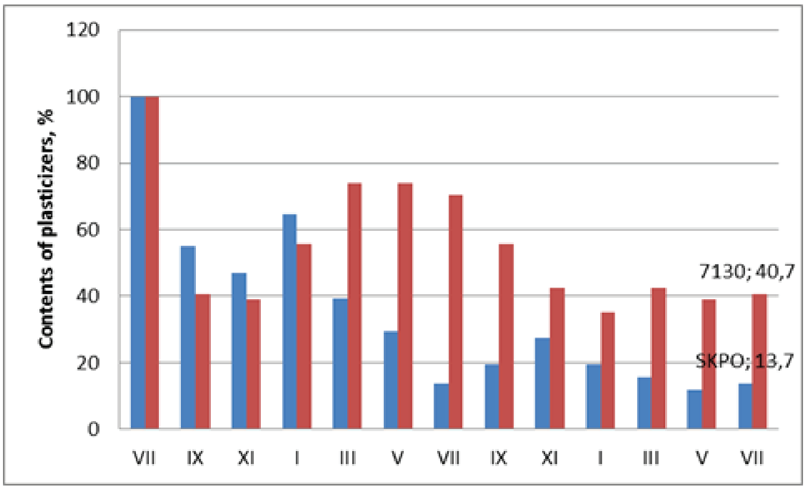

Figure 4: Contents of plasticizers (in percentage terms relative to initial value) in rubbers exposed in oil under natural conditions during 24 months: 1 – SKPO; 2 – 7130.

As an example, we would like to consider studies for determining the warranty period of the rubber seals of the pipeline "Talakan-Vitim". The pipeline has a special construction, it does not contain weld joints in its assembly. The pressurization is provided by rubber seals made from NBR. The analysis of the results of investigation on determining plasticizer contents in the ring material operating in the pipeline showed that after two years of operation plasticizer contents in the rubber was 6 times as low. This must cause degradation of basic operation properties.

4. Conclusion

Elastomers applied as seals, gaskets, collars under the conditions of the North must meet the requirements of frost resistance, oil, and benzene stability. These requirements are somewhat alternative, as the combination of low glass-transition temperature, which determines operability of the polymer as a frost resistance material are, for the most well-known polymers, in even inconsistency with their ability to swell in organic solvents and oils. That is why aiming at compromise combination of the said properties, a significant amount of plasticizers (low-molecular weight substances), which reduce intermolecular interaction in the polymer, raise mobility of all structural elements of the system at low temperature, and, as a consequence, improve its frost resistance, is injected into the material. However, interaction of rubbers with oil media (fuel, lubricants) causes diffusion of a plasticizer from the elastomer material into the contacting medium. Extremely low (to -55°C) temperatures in winter, sharp (to 30°C) alternations of temperature passing through zero in spring and autumn, hot summer, which are characteristic of sharply continental climate of Yakutia, strongly impact diffusion processes and changing of rubber properties as a whole.

Performed investigations showed difficulties of modeling rubber behavior under combined influence of climatic factors and oil medium in the laboratory. Forecasting of rubber units longevity should be based on the material testing under the conditions close to operational ones. From this point of view the climatic polygon constructed at the NEFU can be very interesting, as it allows testing of materials under natural conditions of sharply continental cold climate.

Thus, performance of several series of rubber after exposing in oil in the climatic conditions of Yakutia was analyzed, recommendations on their application have been developed. Choosing the material for production of different seals for the conditions of the North one must use rubbers having significant temperature range of operation. Among these rubbers we can recommend propylen-oxide elastomer, which is highly frost resistant (Tg=-74°C) and has a stable set of operational properties in hydrocarbon media.

Propylene-oxide rubber in addition to frost resistance has several valuable properties: high ozone and weather resistance, high strength characteristics and elasticity. However, for better meeting the requirements for rubber seals it is necessary to reduce residual compression deformation, improve wear and oil resistance of materials based on SKPO. For modifying SKPO rubber layered silicates or clay, CNT, graphene oxide and ultrafine polytetrafluoroethylene (UPTFE) were applied as fillers. All studied rubbers based on SKPO have a unique frost resistance, high abrasion, weathering resistance, they are operable from -60 to + 150°C. Rubbers can be applied in production of seals for automotive, railway transport, heavy mining equipment, seals for double glazing. 4 Russian patents (No 2294346,2007, No 2294341, 2007, No 2493183, 2012, No 2502759,2012), two US patents (US 8,841,370 B1,2014, Wear-resistant rubber based on propylene oxide rubber and ultrafine polytetrafluoroethylene; US 8,822,579 B1, 2014, Frost-resistant rubber based on propyleneoxide rubber and natural bentonites) were received. One of our patents was awarded a diploma of “100 best inventions in Russia in 2013”.

Acknowledgement

This work was supported by the Ministry of Education and Science of the Russian Federation, state assignment no. 11.512.2014.

References

[1] IN. Chersky and VA. Morov, Analysis and prediction of rubber and seals serviceability, in *In Arctic conditions. Kautschuk und Gummi Kunststoffe*, **43**, 128–129, 128-129, 43(6, 1990.

[2] MF. Bukhina, *Kurlyand SK: Low-temperature Behaviour of Elastomers*, Leiden; Boston, VSP, 2007.

[3] S. Vishnitsky and GV. Chubarova, Morozov YL: Development of weatherproof rubber with improved low-temperature and adhesion properties. Rubber and vulcanized rubber, in *Govorova OA*, **26**, 18–20, 26, 1999.

[4] State. GOST270-84 Standard, (1850)., Rubber: method of the determination elastic and tensile stressstrain properties, http://vsegost. com/Catalog/21/2.shtml, .

[5] State. Standard and Rubber. , Method for determination of frost on the elastic recovery after compression, `http://vsegost.com/Catalog/24/24430.shtml`.

[6] State. Standard, Unified system of corrosion and aging protection -vulcanized rubbers: method of testing resistance to attack by corrosive media in limp state, http://vsegost. com/Catalog/35/3586.shtml, .

[7] *GOST 9.024-74 State Standard, Unified system of corrosion and aging protection- rubbers: methods of heat aging stability determination, URL*, http://vsegost.com/Catalog/36/36404.shtml.